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Ionic and Electronic Transport in Gels and Aerogels

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13. ABSTRACT

Organic and inorganic gels, and gel-derivatives such as aerogels and xerogels, find numerous applications in areas such as batteries, fuel cells, photoelectrochemical solar cells, photocatalytic devices, supercapacitors, control-release drug delivery systems, separation techniques, and others. Modern microscopic and electrochemical techniques offer the possibility of understanding structural properties of these systems down to almost atomic level. Most of the applications involve solid-liquid interfaces that occupy a significant fraction of the volume of these materials. This review discusses transport in three heterogeneous systems with important applications: solutions of ionic polymers, polymeric gels and aerogels.

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Ionic and Electronic Transport in Gels and Aerogels

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Introduction

Mechanisms of charge transfer can be quantitatively correlated with structural information through application of techniques such as atomic probe microscopies and time-resolved conductivity measurements. The advances in sequencing of natural polymers such as nucleic acids and proteins, and advances in synthesis of supermolecular structures, has made it possible to correlate mechanisms of charge transport across such systems with the molecular structure. The culmination of these efforts is the degree of understanding that is being displayed of the detailed charge transport mechanisms in the photosynthetic reaction centers [1-4].

Structures of considerable interest to electrochemists are those that result in non-crystalline heterogeneous environment in which structures cannot be simply characterized in terms of sequence of the elementary units or translational symmetry of unit cells.

This review discusses transport in three heterogeneous systems with important applications: solutions of ionic polymers, polymeric gels and aerogels. Aerogels are derived from gels by removing the solvent with minimal disruption of the gel network through application of supercritical drying. The applications of concern here are those where solvent is replaced with electrochemical media in which electrochemical or photoelectrochemical reactions take place.

We conclude the review by describing some applications that are of interest to electrochemists, in which gels and aerogels play prominent role. These include liquid-junction photovoltaic devices, electrochemical capacitors and lithium batteries.

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Theoretical Background

Theories of charge transport in gels and aerogels can be approached from two opposite directions: mean-field, effective medium approaches that treat the medium as an effective dielectricum, and network approaches that attempt to calculate transport properties from given structural properties. The dividing line is not always clear but with recent advances in computer power that enable calculation of transport in complicated networks, the two approaches start to converge.

Within the context of conductivity of porous rocks saturated with electrolytes, Cohen [5] has shown that the electrical properties of an inhomogeneous material are invariant with the scale of the inhomogeneity at finite frequencies as long as they are determined by the bulk properties of the constituents, and the wavelength of the electromagnetic fields used is much longer than any characteristic length scale of the system.

We will discuss first mean-field approaches followed by network simulations and conclude this section with some recent attempts to converge these approaches. A good example of the mean-field approach that was applied to nucleic-acid solution and is directly connected to transport in other polyelectrolytes, can be found in [6] and is based on the Poisson-Boltzmann distribution.

Let us approximate the free energy of a solution of macro-ions, counterions, and added salt by the following simple functional of the ion concentrations:

$$F_{PB}(\{n_i\}) = \int dr \{\frac{1}{2}\rho\Psi + kT\sum_i n_i \ln(n_i/n_0)\} \quad (1)$$

The second term is the mean-field entropic free energy of the ions, with n_i being the concentration of the ith ion species carrying charge $z_i e$ (n_0 sets the zero of the potential). The first term is the electrostatic energy, with the charge density $\rho(r)$ being the sum of charge densities of the macro-ions and the mobile ions:

$$\rho(r) = \rho_{macro}(r) + \sum_i z_i e n_i(r) \quad (2)$$

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The local electrostatic potential is $\Psi(r)$. The charge density and the potential are related by Poisson's equation, $\nabla^2\Psi = (4\pi/\varepsilon)\rho(r)$, where ε is the dielectric constant of the continuum - the aqueous medium in which the ions are dissolved. Minimization of eq. 1 with respect to the ion concentrations leads to the condition that they obey the Boltzmann distribution. More explicitly, using Poisson's equation, we obtain:

$$\nabla^2\psi = -(\frac{4\pi e n_0}{\varepsilon})\sum_i z_i \exp(-z_i e\psi/kT) \qquad (3)$$

for the potential outside the surface of the macro-ions. This nonlinear differential equation, which is known as the Poisson-Boltzmann (PB) equation, must be solved under the boundary condition that the electric field $\vec{E} = -\nabla\Psi$ at the surface of a macro-ion be consistent with its fixed charge density σ.

A specific example of this approach with many applications in the polyelectrolyte and electrochemical literature is Manning's theory with a line charge model [7-9] in which the counterion self-diffusion coefficient depends on the dimensionless charge density, λ, given by:

$$\lambda = \frac{e_0^2}{4\pi\varepsilon\varepsilon^\circ bkT} \qquad (4)$$

where e_0 is the elementary charge, ε is the dielectric constant of the solvent, ε° is the permittivity of vacuum, b is the length of the polyion per ionized group (charge spacing), k is the Boltzmann constant, and T the absolute temperature.

Manning's theory treats polyions as infinitely long line charges. Counterions are assumed to condense onto the polyion chain as required to avoid exceeding the critical charge density, λ_c (for monovalent counterions $\lambda_c = 1$). These condensed counterions are inside the hydration layer; therefore, their mobility is that of the polyion, usually negligible in comparison with the mobility of free counterions. Uncondensed counterions and coions are subject to Debye-Hückel interactions with the polyions.

Depending on the charge density of the polyion, the ratio of the diffusion coefficient of the counterion in the polyelectrolyte solution to that in solution without polyelectrolyte is [8]:

$$D_{PE}/D_0 = 1 - 1/3 \times A(\lambda; X) \qquad (5)$$
$$\text{for } \lambda < 1$$

$$D_{PE}/D_0 = 1 - 1/3 \times A(1; \lambda^{-1}X) \qquad (6)$$
$$\text{for } \lambda > 1$$

where D_{PE} and D_0 are diffusion coefficients of counterions in solutions with and without polyelectrolyte, respectively, X is the ratio of the concentration of polyelectrolyte to the concentration of added univalent salt, $X = C_{PE} / C_{SB}$, and $A(\lambda; X)$ is given by:

$$A(\lambda; X) = \sum_{m_1 = -\infty}^{\infty} \sum_{m_2 = -\infty}^{\infty} [\pi \lambda^{-1}(m_1^2 + m_2^2) + 1 + 2X^{-1}]^{-2}$$
$$(m_1, m_2) \neq (0,0)$$

$$(7)$$

where m_1 and m_2 are integers.
In salt-free solution, $X \to \infty$,

$$D_{PE}/D_0 = 1 - 1/3 \times A(\lambda; \infty)$$
$$\text{for } \lambda < 1 \qquad (8)$$

$$D_{PE}/D_0 = \lambda^{-1} \times [1 - 1/3 \times A(1; \infty)]$$
$$\text{for } \lambda > 1 \qquad (9)$$

where $A(\lambda; \infty)$ can be obtained from eq. 7 by setting $X^{-1} = 0$. Numerical evaluation of the series results gives $A(1; \infty) = 0.40$, and therefore:

$$D_{PE}/D_0 = \lambda^{-1} [1 - 1/3 \times 0.40] = 0.867 \times \lambda^{-1}$$
$$\text{for } \lambda > 1 \qquad (10)$$

As one can see from eqs. 4-10, measurements of counterion diffusion coefficients yield the charge spacing, b, of the polymer, and thus could be used for structural characterization.

Other applications of the Poisson-Boltzmann equation in calculating properties of polyelectrolyte systems with different geometries are given in references [10-14]. Equation 3 can be used to calculate the quantity $1 - f$, the number fraction of counterions in the deionized solution that have an energy of attractive electrostatic interaction with the macroion greater than kT. These counterions are considered to neutralize the anionic sites of the macroion, and their transport is limited by the diffusion of the macroion, which has a diffusion coefficient two orders of magnitude less than that of the free counterion. The fraction of ions, f, is free to diffuse. The value of f is identified with the D/D_0-value in Manning's theory and with the experimentally determined transport ratio in deionized solution.

Network simulation of transport in gels is often associated with simulation of diffusion in restricted media. Let us first correlate hopping mechanisms with diffusion properties. For one-dimensional hopping in unrestricted media, the probability that a walker is on site i after n steps is given by:

$$P_n(i) = 1/2\, P_{n-1}(i-1) + 1/2\, P_{n-1}(i+1) \qquad (11)$$

where $t = n\tau$, $x = ia$, and τ and a are the hopping time and distance to the adjacent site.

$$P_n(i) = aP(x,t) \qquad (12)$$

$$P(x,t) = 1/2 P(x+a, t-\tau) + 1/2 P(x-a, t-\tau) \qquad (13)$$

$$\frac{1}{\tau}[P(x,t) - P(x,t-\tau)] = \frac{a^2}{2\tau}[P(x+a,t-\tau) - 2P(x,t-\tau)$$
$$+ P(x-a,t-\tau)]a^{-2} \qquad (14)$$

Expand
$P(x,t-\tau)$ and $P(x\pm a, t-\tau)$ in Taylor series and take the limit at $a \to 0$, and $\tau \to 0$.

Define $D = a^2/2\tau$ as the diffusion coefficient to obtain:

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P(x,t)}{\partial x^2} \qquad (15)$$

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Diffusion of solutes in the gels is determined by the interactions of diffusing solute molecules with the solvent and the polymer molecules. The chemical nature of the gel plays a specific role. It is often approximated in terms of general effects such as geometrical obstructions and hydrodynamic drags. In many cases the hydrodynamic influence is found to be secondary to the steric hindrance. The relevant factors are the concentration of the polymer gel, the solute size, the geometry of the chain: i.e., the shape, thickness and stiffness of the chains.

In terms of simulation, the most common approach is diffusion in the spaces in random suspension of fibers [15,16]. Often the scaling derived from Fick's second law, eq. 15,

$$<r^2(t)> \propto t \qquad (16)$$

does not hold and instead, the scaling is generalized to:

$$<r^2(t)> \propto t^{(2/d_w)} \qquad (17)$$

where d_w is the anomalous diffusion coefficient; for restricted diffusion $d_w > 2$ [17].

Diffusion of latex spheres in polyamide gels was studied by using quasi-elastic-light- scattering [18]. Three regimes were identified. At very short times, the diffusion process is normal and the influence of the polymer is negligible. At moderate times the diffusion becomes anomalous. At large delay times, the diffusion returns to be normal as long as the monomer concentration is below the gelation point. The change from the second to the third regime depends on the monomer concentration and was spatially characterized in terms of a crossover length between normal and anomalous diffusion that diverges at the gelation point. NMR studies of diffusion of water in polyacrylamide gels [19] have detected anomalous diffusion in the form of time-dependent diffusion coefficient in the neighborhood of the gel transition.

For diffusion of tracers of radius R diffusing around random distribution of obstacles of density v, Netz et al. [16] and Johanson et al. [20] arrived at the following expression:

$$\frac{D}{D_0} = e^{-a} + a^2 e^a E_1(2a) \qquad (8)$$

where E_1 is the exponential integral function, D_0 is the diffusion coefficient without obstacles, and a is related to the volume excluded for diffusion.

To account for the low-temperature behavior of the electronic conduction processes in disorder materials, one needs to consider situations in which the scattering of the electrons by the atoms is strong, giving rise to localization of the electron wavefunctions to form "Fermi-Glasses" [21]. In such systems, when the Fermi energy (E_F) is in the range of energies where states are localized, two mechanisms of conduction are possible: normal Arrhenius-type conduction, predominant at high temperatures (or when ε is small), with the following temperature dependence:

$$\sigma = \sigma_{min} \exp(-\frac{\varepsilon}{kT}) \qquad (19)$$

where σ_{min} is the value of σ at $E = E_c$, E_c is the energy threshold for localized states, and $\varepsilon = E_c - E_F$.

The second possible mechanism is thermally activated hopping conduction in which the rate-determining step is the hopping of an electron from a state below the Fermi level to a state above it. For such systems the hopping distance will be temperature dependent, and at sufficiently low temperature, the three dimensional conductivity will behave as:

$$\sigma = \sigma_0 \exp(\frac{T_0}{T})^{\frac{1}{4}} \qquad (20)$$

where T_0 is a constant.

When electron-electron interactions are taken into account, Shaklovskii and Efros [22] showed that a quasigap appears in the density of states at the Fermi level, and that the resulting conductivity exhibits a Coulomb-Gap Variable Range Hopping that takes the following form:

$$\sigma = \sigma_0 \exp(\frac{T_0}{T})^{\frac{1}{2}} \qquad (21)$$

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Solutions of Ionic Polymers

The inference of ionic interactions from transport data requires measurements over a wide range of concentrations, extending to solutions of very low ionic strength, nominally without added electrolyte. Various techniques have been used for determination of diffusion coefficients of simple ions in solutions of ionic polymers (as known as polyelectrolytes), including radioactive tracer [23-27] and FT NMR [28-32]. The effectiveness of electroanalytical methods, mainly steady-state voltammetry at microelectrodes, but also chronoamperometry and conductance measurements for transport studies in polyelectrolyte systems has been demonstrated for several systems [33-51]. Small microelectrode size (diameter in the range of several micrometers) yields steady-state voltammograms on time scales of seconds and makes measurements possible in resistive media, such as solutions without supporting electrolyte. In addition, the steady-state current, i_s, at microelectrodes is proportional to the flux of reactant, as shown by eq. 22 for a disk microelectrode

$$i_s = 4nFCDr_d \qquad (22)$$

where C is the concentration of electroactive species r_d is the radius of the microelectrode, n is the number of electrons transferred, and F is the Faraday constant. Thus the voltammetric signal is very sensitive to changes in the value of the diffusion coefficient. This method has advantages of simplicity, low cost, and very high throughput in comparison with other methods (NMR, radioactive tracer method) used to study these systems.

It has been shown that the transport rate of the singly charged cations of hydrogen and thallium, in solution of the synthetic polyelectrolyte poly(styrenesulfonic acid), PSSA, without supporting electrolyte, is only one-third that in solution without polyelectrolyte [33-35]. This result agrees well with the predictions of the two major theories for polyelectrolytes, Manning's linear charge model and the Poisson-Boltzmann cylindrical cell model described above.

A phenomenological equation for describing the results of measurements of diffusion coefficients in

polyelectrolyte systems has been proposed [34]. Over the entire range of ionic strengths, the diffusion coefficient of a counterion in polyelectrolyte solution, D, normalized by the diffusion coefficient of the same ion in solution without polymer, D_0, should behave as follows:

$$\frac{D}{D_0} = \frac{(\alpha / \gamma + 1)}{1 / \gamma} \qquad (23)$$

where γ is a ratio of the concentration of an univalent salt to the equivalent concentration of the ionic polymer ($\gamma = C_{SE}/C_{PE}$), and α is an empirical factor equivalent to the ratio of the diffusion coefficient of a couterion in polyelectrolyte solution to its value in the absence of polyelectrolyte, both in solution without any electrolyte. The parameter α can be determined empirically, by simple calibration curves in the presence and absence of polyelectrolyte [34]. Equation 23 permits prediction of an influence of added electrolyte on diffusion of small counterions in a solution of ionic polymer.

Experimental results for four equivalent concentrations of PSSA have been compared with predictions of that phenomenological equation, Figure 1, and it has been found that experimental and calculated values are identical within an experimental error.
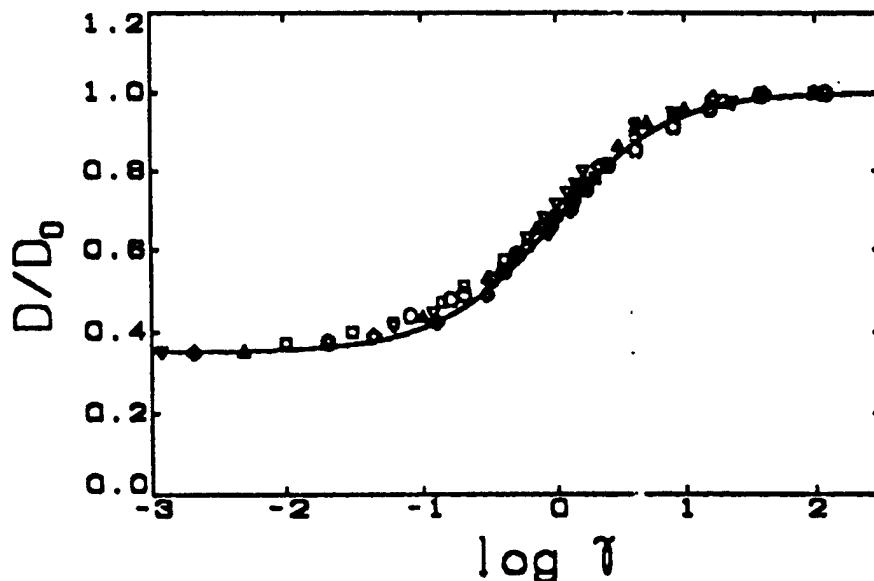

Figure 1. Calculated (solid line) and experimenta transport ratio, D/D_0, for various ratios o.

electrolyte (LiClO$_4$) to hydrogen ion concentration ($\gamma = C_e / C_h$) for reduction of hydrogen ion in: (O) 0.05, (Y) 0.1, ($\triangle$) 0.2, ($\lozenge$) 0.47, (∇) 1.05 mM PSSA solution. (Reprinted with permission from ref. 34. Copyright 1994 American Chemical Society.)

Effects of size and identity of ions of electrolyte added to a solution of a polymer have been studied. No specific influence of the anion of the supporting electrolyte on transport of counterions in PSSA solutions has been found. From a group of several cations (Li$^+$, Na$^+$, K$^+$, Cs$^+$, TMA$^+$ (tetramethylammonium), and TEA$^+$ (tetraethylammonium)), only TEA$^+$ shows preferentially strong interactions with PSSA. Strong influence of a charge of a cation of supporting electrolyte on transport properties of counterions in polyelectrolyte solutions has been demonstrated [34]. Figure 2 presents the dependence of the normalized diffusion coefficient of hydrogen counterion on concentration of electrolytes with various cation charges (+1, +2, and +3).
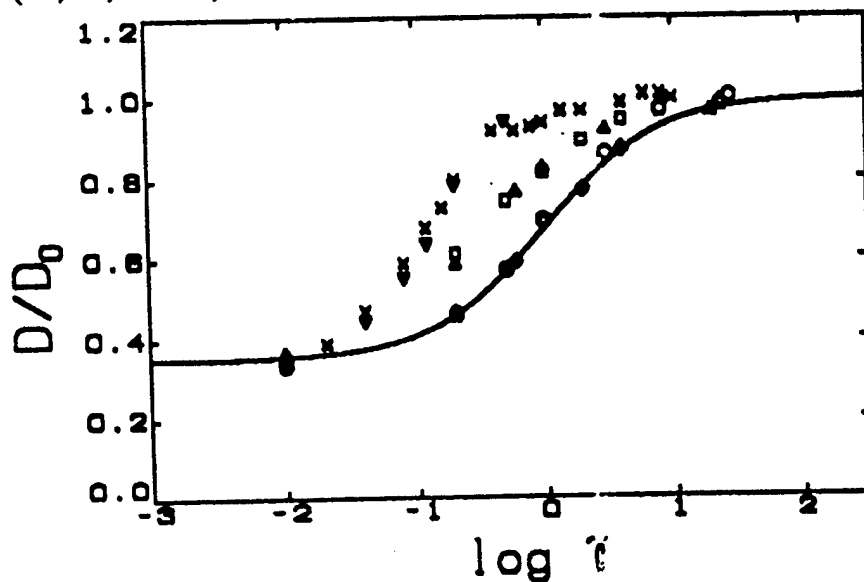

Figure 2. Calculated (solid line) and experimental transport ratio, D/D_0, for various ratios of electrolyte to hydrogen ion concentration (γ) for reduction of hydrogen ion in 0.1 mM PSSA solution. Dependence on charge of supporting electrolyte cation: (O) NaCl, ($\lozenge$) KCl, ($\triangle$) MgCl$_2$, (Y)

It indicates the stronger interactions of polyion with more highly charged cations than with monovalent cations. Very similar phenomenon has been found for multicharged counterions. It has been shown for metal cations such as Pb^{2+} and Cd^{2+} that their interactions with ionic polymers are much stronger that for monovalen cations such as H$^+$ and Tl$^+$ [35].

Comparison of results for transport of ^{205}Tl(I) in PSSA solutions from voltammetric experiments and pulsed-field-gradient spin-echo NMR (PFGSE NMR), a well-developed method for transport studies, has shown that the gradient diffusion coefficient measured by voltammetry is identical with the self-diffusion coefficient from PFGSE NMR [36]. The values agree over a wide range of electrolyte concentration within experimental uncertainty, despite the different principles on which the two methods are based.

It has been shown that steady-state voltammetry with microelectrodes can be used successfully for the study of transport of counterions in mixed solvent solutions of polyelectrolytes [38]. The interactions between poly(styrenesulfonate) ion and thallium(I) counterion in solutions without added electrolyte were found to depend on the bulk dielectric constant of the solvent. The normalized diffusion coefficient of Tl(I) in a solution of poly(styrenesulfonic acid) changed in proportion to the change in the value of dielectric constant of the solvent. This dependence was observed for ethanol-, methanol- and 1,4-dioxane-water mixtures. For example, in a solution of ethanol-water mixture of dielectric constant $\varepsilon = 25$, the diffusion coefficient of Tl(I) in PSSA was found to be one-tenth the value in simple acid solution, which means that the transport of Tl(I) in PSSA was 10 times slower than in p-TSA. This is much lower than the value of 0.35 obtained in aqueous solution, $\varepsilon = 79$, for the same system [38]. Similar changes in transport properties of counterions in polyelectrolyte solutions with changes in dielectric constant of solvent are predicted by Manning's theory, see eqs. 4-10. The slope of average dependence of normalized diffusion coefficient of Tl(I) in PSSA solution for various compositions of

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investigated solvents is 0.00449, while the theoretical dependence has the slope of 0.00426. Although these results were obtained for only one kind of counterion, Tl(I), this methodology can be used to study the transport properties of other electroactive mono- and multivalent counterions under variety of experimental conditions, in solutions of various solvents and polyelectrolytes, including naturally occurring, biological polyelectrolytes.

To test the predictive power of Manning's theory, and to analyze experimental results in light of existing models, a group of anionic polymers that have a range of charge separation distances, and hence of charge densities has been studied [37,39]. Transport of monovalent cations was investigated in solutions of biological polyelectrolytes shown in Figure 3, the sodium (or potassium) salts of anionic polysaccharides ι-, κ-, λ- carrageenan, dextran sulfate and chondroitin sulfate (with the charge separation distance, b, of 0.47, 1.01, 0.48, 0.25, and 0.58 nm, respectively), by steady-state voltammetric reduction of the probe ions Tl^+ and H^+ at mercury film and platinum disc microelectrodes, respectively. Figure 4 presents experimental transport ratio, D/D_0, as a function of the charge separation distance together with values calculated according to Manning's theory (eqs. 4-10) and the Poisson-Boltzmann model (eq. 3). The results generally agree better with Manning's theory for $\lambda > 1$, whereas the single result for polyion with $\lambda < 1$ (κ-carrageenan) appears to lie closer to the prediction of the Poisson-Boltzmann model [39].

kappa-Carrageenan, R = H   Dextran   Sulfate
iota-Carrageenan, R = SO₃⁻

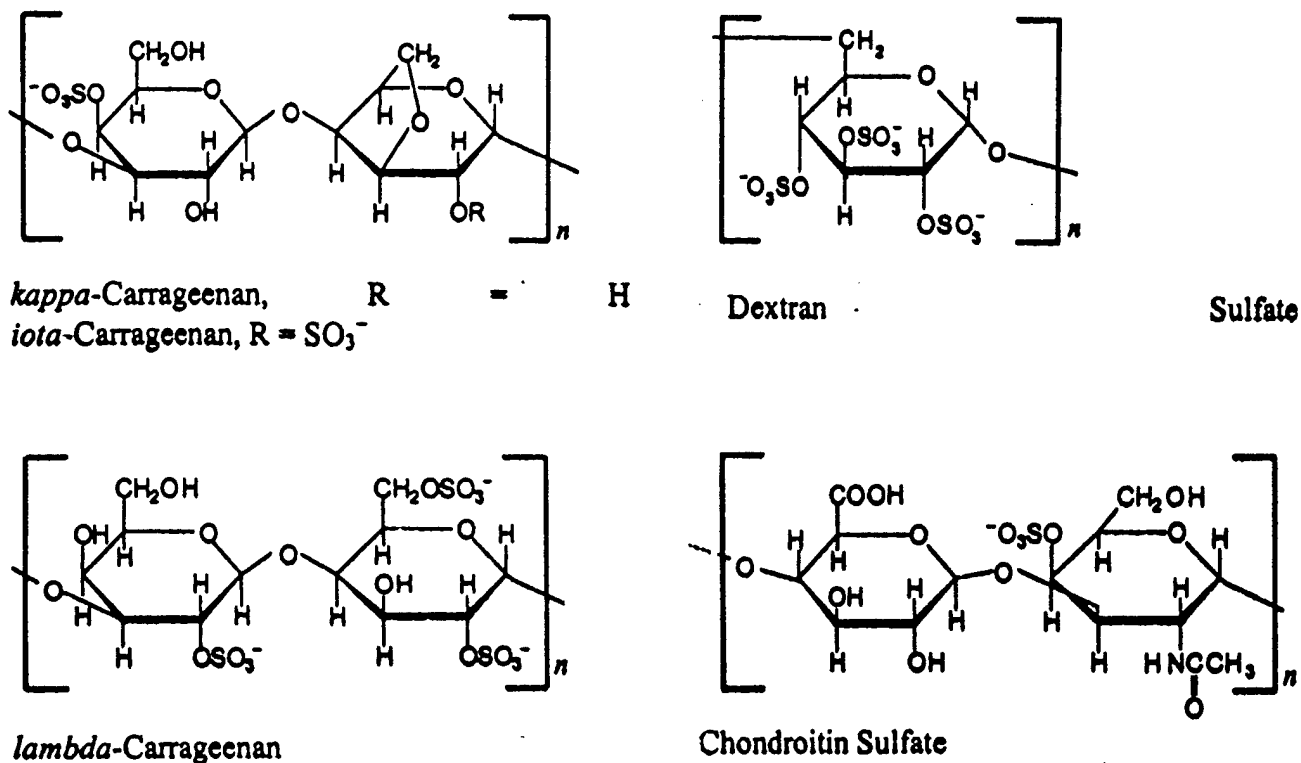**lambda**-Carrageenan   Chondroitin Sulfate

Figure 3. Repeating monomer units of *kappa-*, *iota-*,
lambda-carrageenans, dextran sulfate, and
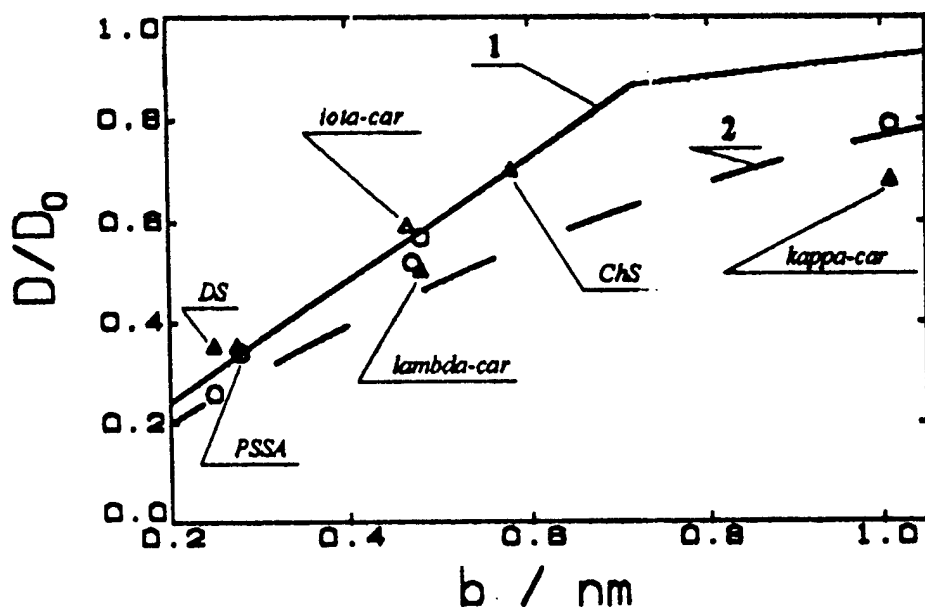chondroitin sulfate.

Figure 4. Transport ratio, D/D_0, as a function of the
charge separation distance, b, according to
Manning's (1) and the Poisson-Boltzmann
(2) model, together with experimental D/D_0-
values for Tl^+ ($\triangle$) and H^+ (O) in
polyelectrolyte   solutions   without

electrolyte. (Reprinted with permission from ref. 39. Copyright 1998 American Chemical Society.).

As shown by Manning's theory, measurements of counterion diffusion coefficients yield the charge spacing, b, of the polymer and thus should reveal the conformation of a polyion such as the coil, helix or multiple helix. Conformation of polyions, both naturally occurring and synthetic, critically influences their properties, including chemical reactivity [10]. It has been shown that voltammetric measurements of diffusion coefficient of counterions can be used together with Manning's theory to obtain values of charge spacing for an anionic polymer to identify the coil-to-helix transition [40,42]. The experimental example was the transformation from coil to double helix of the polysaccharide κ-carrageenan induced by a decrease in temperature. The technique employed, steady-state voltammetry, is simple, robust, rapid, and inexpensive in comparison with conventional methods such as circular dichroism, NMR, and X-ray diffraction. It can be employed in unmodified solutions of polyelectrolytes, and provides quantitative structural information. Figure 5 shows dependence of transport properties of electroactive probe ion, Tl^+, on a conformational form of κ-carrageenan, and comparison of voltammetric and circular dichroism results for the same system. It has been also shown [41] that very simple conductance experiments can reveal coil-to-helix transition of an anionic polymer, that those results are identical to voltammetric data [42], and they can be used for determination of the charge spacing in conformers.
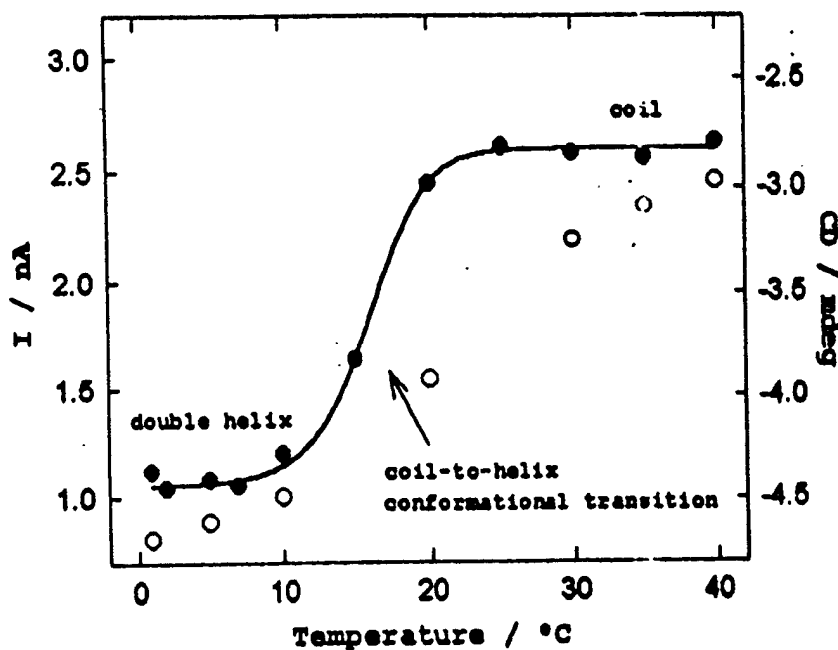
Figure 5. Dependence of the normalized (*versus* the limiting diffusional current at 20 °C) reduction current of 0.3 mM Tl⁺ (●) and circular dichroism response at 300 nm (O) on temperature of 20 mM *kappa*-carrageenan solution. (—) Best fit of voltammetric results. (Reprinted with permission from ref. 54. Copyright 2000 American Chemical Society.)

Polymeric Gels

The widely accepted topological definition of a gel is a three-dimensional network constituted of basic elements connected in some way and swollen by a solvent. As a rule, only systems wherein the solvent is the major component are considered to be gels. A gel possesses the unique property of incorporating and retaining a proportion of liquid molecules outweighing by far the proportion of the basic, added component. In some cases a gel can contain up to 99% solvent. This is a rather unusual way in which large amounts of liquid can be maintained "solid", and therefore, gels possess many advantages characteristic of both the liquid and solid state of matter [55-58].

It has been shown that electroanalytical techniques can be used effectively in transport studies in polymeric gels [47-51,59-61]. Those techniques require only simple and inexpensive equipment and can be quickly completed. The measurement of steady-state transport-limited currents is robust, it permits studies under very wide ranges of ionic strengths and temperatures, and it allows accurate and precise determination of diffusion coefficient, as described by eq. 22.

The diffusion coefficient of the uncharged probe TEMPO (2,2,6,6,-tetramethyl-1-piperidinyloxy) has been determined in two biopolymeric gels, agarose and iota-carrageenan [47]. For low concentration of the polymer (approximately 1%) the three-dimensional structure of the polymeric network does not influence transport properties of this probe, and it does not change or modify electrode processes at platinum microelectrodes. For higher concentrations of the biopolymer and consequently shorter distances between polymeric segments in the gel, the diffusion coefficient of TEMPO decreased. Additionally, macroscopic viscosity of agarose and iota-carrageenan gels does not influence diffusion of small molecules and ions, and for low concentrations of the polymer, the diffusion coefficient of those species depends on the composition of the solution immobilized in the gel network, or in other words, on local microscopic viscosity of the system [47].

For the charged electroactive probe, Tl^+, it has been shown that in the neutral gel, agarose, thallium reduction is identical to that in aqueous solutions, with the same effects of migration in systems of low ionic strength [47]. This voltammetric method could be used for the estimation of low concentrations of ions in uncharged gels. In the polyionic gel, iota-carrageenan, it has been shown that electrostatic interactions between the polyanion and thallium cation significantly change the transport properties of Tl^+. The change of the diffusion coefficient of the Tl^+ probe in the iota-carrageenan gel was similar to that predicted by Manning's theory for a monovalent counterion in solutions of the double helix form of iota-carrageenan, with an assumption of the linearity of the polyion [47].

It has been demonstrated for polyacrylate gels [48] that the diffusion of small uncharged molecules is

mainly influenced by the composition of the solution immobilized in the gel network. Therefore, transport properties of uncharged molecules in such systems can be predicted based on the solution composition, mainly on its viscosity. However, transport properties of ions in polyacrylate gels depend strongly on the charge density of the polymer. Since the amount of a strong base added to PAA determines the charge separation distance and charge density of the polyanion, the strength of electrostatic interactions between simple ions and polyions in PAA gels depends on the degree of neutralization of the polyacid. For a very low degree of neutralization of PAA, and consequently for very low charge density of that ionic polymer, the diffusion coefficient of the probe cation, Tl^+, is identical to that in solution without polymeric network. As the charge density of polyacrylate network increases with addition of NaOH, the diffusion coefficient of the thallium probe cation decreases due to electrostatic interactions with the polymeric network. While is has been shown previously that the low concentration of an ionic polymer in a gel does not significantly influence transport properties of uncharged molecules in that medium [47], the experimental results for the probe cation, Tl^+, show for the first time the dependence of transport properties of the probe cation on the wide range of charge densities of anionic gels. Since the experimental results suggest that transport properties of ions, both counter- and co-ions, in ionic polymeric gels can be modified by selection of appropriate charge density of the polymer, they might have significant practical consequences in gel-based separation techniques and in the development of gel-based sensors. Additionally, polyacrylate gels with their wide range of available charge densities can mimic behavior of other ionic gel systems, and can be used as simple and inexpensive models.
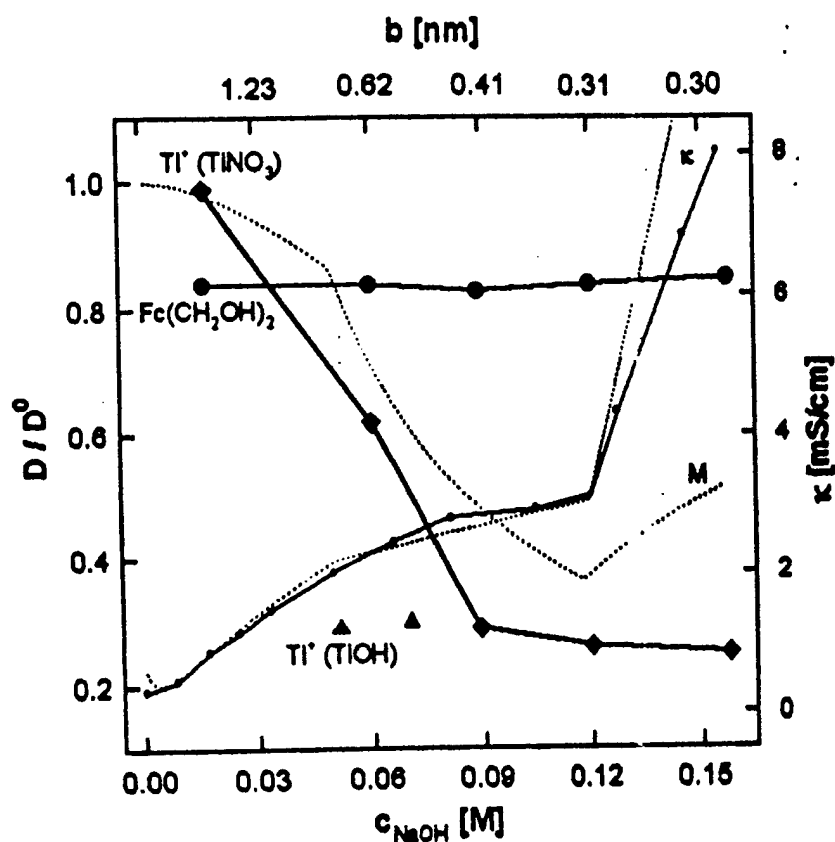
Figure 6. Dependencies of normalized diffusion coefficients determined voltammetrically (solid lines and symbols) for chosen electroactive probes in sodium polyacrylate gels with respect to concentration of added NaOH. The thinner solid line presents appropriate conductometric titration curve. The dotted lines refer to theoretical predictions according to Manning's theory (M) and calculated conductometric titration curve (κ). (Reprinted with permission from ref. 48. Copyright 1999 American Chemical Society.)

Figure 6 summarizes experimental and theoretical results, based on a new model [48], for voltammetric and conductometric measurements by

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presenting the dependencies of normalized diffusion coefficients of uncharged and charged probes and the conductivity of gels on concentration of added base. The new theoretical relation for the charged probe cation is compared with the theoretical predictions according to Manning's line charge theory for monovalent counterions in solutions of ionic polymers. The relatively large differences between theoretical predictions and experimental results for polyacrylate gels observed for large concentrations of NaOH are probably due to stronger electrostatic interactions in three dimensional networks of ionic gels than in polyelectrolyte solutions.

An interesting phenomenon has been observed in thallium polyacrylate gels from PAA neutralized (and gelled) by TlOH; the diffusion coefficient of thallium counterion was very low even for a low degree of neutralization of the polyion and its value was close to that of Tl^+ probe in high-charge density sodium polyacrylate gels (see Figure 6) [48]. This result illustrates how strongly transport properties of thallium cations depend on their role in polymeric network (probe ions or native counterions) and it shows that polyacrylate gels can be treated as three dimensional networks consisting of negatively charged polyacrylate chains linked by strongly immobilized metal counterions (Na^+ or Tl^+) of the strong base used for their neutralization and swollen by a solution (or solvent). This is the first direct experimental evidence of such a structure.

The new method proposed for calculation of the conductivity of polyacrylate gels [48], based on the summation of partial conductivities of all types of ions and coupled to chemical (acid-base) equilibrium is very general, and it can be applied for any analogous ionic polymer systems to predict their conductometric properties for any degree of neutralization or any charge density of polyion. Additionally, this model can be applied not only for hydrogels but for gels based on mixed or non-aqueous solvents. Therefore, the method may be extremely useful to predict conductivities of non-aqueous polyionic gels for gel-based batteries or other power sources. The theoretical predictions for conductivity of polyacrylate gels agree well with experimental measurements especially for nonzero values of counterions mobility along the polyions. Therefore, this approach can be used for the

determination of diffusion coefficient of counterions condensed onto polyion chains (not only free to diffuse in solution).

Some polymeric gels, mainly polyelectrolyte gels, undergo discontinuous volume change transitions as a function of environmental variables such as pH or temperature [62,63]. Volume changes during such transitions may be quite significant, some exhibiting changes that are very large. The phase transition of a polymer gel results from a competitive balance between a repulsive force that acts to expand the polymer network and an attractive force that acts to shrink the network. The most effective repulsive force is the electrostatic interaction between similarly charged polymer strands, which can be imposed upon a gel by introducing ionization into the network. Attractive interactions can be van der Waals, hydrophobic interaction, and hydrogen bonding. Because polyelectrolyte gels exhibit such dramatic changes in their structure by responding to environmental changes, they have been increasingly studied as vehicles for applications such as drug delivery [64-66], separation media [67], and the construction of sensors [68-70]. In such applications, the knowledge of diffusion coefficients of ions and molecules as a fundamental measure of molecular mobility and electrostatic interactions is of great importance. It has been shown that electroanalytical techniques can be used successfully to monitor transport of ions and molecules in polymeric gels undergoing discontinuous volume phase transitions [50,51,71]. Transport of ions and molecules has been studied in thermoresponsive gels of poly(N-isopropylacrylamide-co-acrylic acid), NIPA-AA. The NIPA-AA hydrogels undergo a discontinuous volume phase transition at 45 °C; this transition results in a release of approximately 40% of the solution mass from the gel phase [51]. Diffusion coefficients of electroactive probes in gels under a wide range of experimental conditions have been determined from steady-state voltammograms, according to eq. 22, or using normalized chronoamperometry and he following relation for a disk microelectrode [72,73]:

$$i/i_s = [1 + (2r_d / \pi \sqrt{\pi D t})]$$ (24)

where i is the current at time t, i_s is the steady-state current, D is the diffusion coefficient of electroactive species, and r_d is the radius of the microelectrode. Similar diffusion coefficients for 1.1'-ferrocenedimethylanol, $Fc(MeOH)_2$, in NIPA-AA gels were obtained by either electroanalytical technique at temperatures lower than 20 °C [51]. The uncertainty in the $Fc(MeOH)_2$ concentration in the gels, resulting from the discontinuous volume change transition, necessitated the use of concentration independent chronoamperometric data, eq. 24, to obtain reliable diffusion coefficient values for $Fc(MeOH)_2$. As indicated by results of Figure 7, for temperatures above the volume phase transition, changes of concentration of $Fc(MeOH)_2$ are detected in a copolymeric collapsed phase.
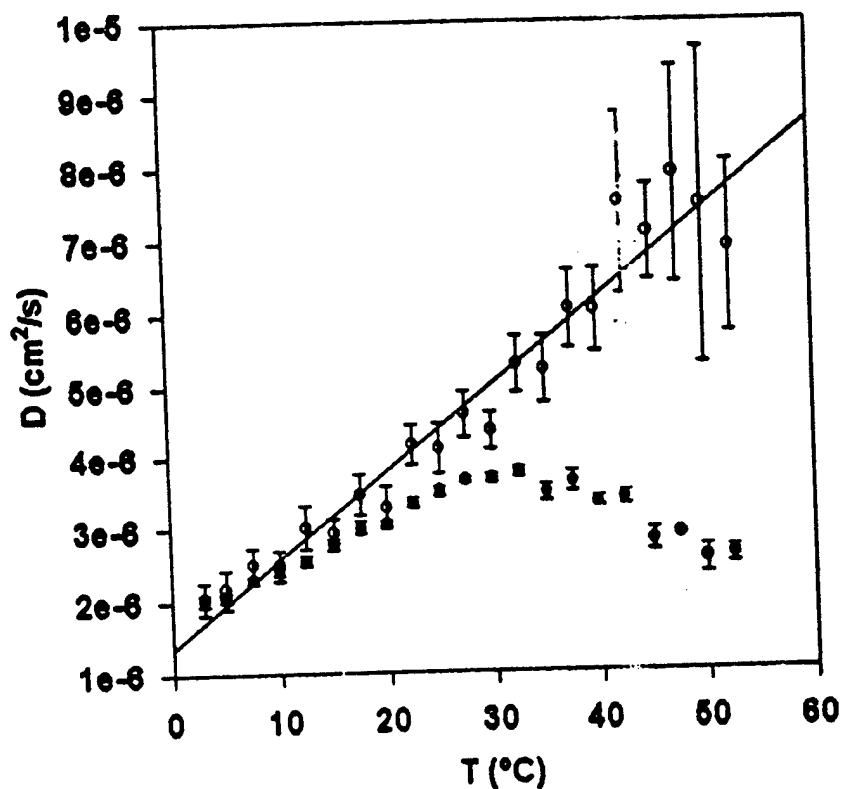

Figure 7. Temperature dependence of the $Fc(MeOH)_2$ diffusion coefficient in a 5% (w/v) NIPA-AA gel as determined by normalized chronoamperometry (O) and steady-state voltammetry (●). The line on the graph

The enormous macroscopic viscosity of NIPA-AA hydrogels had no significant effect on transport of small probe molecules [51]. For example, as shown by Table 1, in a 4% (w/w) NIPA-AA gel, the viscosity is approximately six orders of magnitude greater than the viscosity of aqueous solution. However, the diffusion coefficient of $Fc(MeOH)_2$ has only decreased by a factor of two compared to the diffusion coefficient of $Fc(MeOH)_2$ in aqueous solution, while for an ideal system, according to the Stokes-Einstein equation, the diffusion coefficient should be inversely proportional to the viscosity of that system.

Table 1. Viscosity and Diffusion Coefficients of $Fc(MeOH)_2$ in Various NIPA-AA Gels [51].

Medium	D (cm^2 s^{-1}) @ 25 °C [a]	η (cP) @ 24 °C
Aqueous Solution	6.3×10^{-6}	9.4×10^{-1}
1% NIPA-AA	5.2×10^{-6}	2.0×10^{4}
2% NIPA-AA	4.3×10^{-6}	2.0×10^{5}
3% NIPA-AA	3.6×10^{-6}	2.3×10^{6}
4% NIPA-AA	3.9×10^{-6}	5.6×10^{6}

[a] $[Fc(MeOH)_2]$ = 2 mM; $[LiClO_4]$ = 0.1 M.

This difference illustrates the distinction between macroscopic and microscopic viscosity; a heterogeneous environment exists in these gels, which allows a solute to easily diffuse within a solution encapsulated in the pores of a swollen and semi-rigid polymer network. The observation that there is only

slight resistance to the diffusion of Fc(MeOH)$_2$ through the polymer network indicates the potential of these gels to be used as semi-rigid electrolytes for electrochemical applications. A new model for description of transport in polymeric gels in their swollen state has been proposed [71]. The modified equation taking into account the "obstruction effect" and "hydration effect" was proposed, and this equation successfully predicated the diffusion coefficient of TEMPO in the NIPA-AA gels.

Poly(N-isopropylacrylamide-*co*-acrylic acid) can be swollen by organic solvents [50]. The electrooxidation of methanol at platinum microelectrodes in NIPA-AA gels has been studied as a function of temperature. Diffusion coefficients of methanol in NIPA-AA gels of various copolymer concentrations were determined from the steady-state voltammetric currents over the temperature range 5 - 55 °C. Transport parameters (diffusion coefficients and activation energies of diffusion) were compared to those for undiluted methanol, and related to the transport properties of uncharged probe molecules of Fc(MeOH)$_2$ in both liquid and gel media. Diffusion of uncharged species, methanol and Fc(MeOH)$_2$, in the gels was as fast as in liquid media. Activation energies of diffusion for methanol and Fc(McOH)$_2$ in the gels were smaller than those observed in liquid media, they did not depend on the copolymer concentration in the range 1.3 – 2.5 %. The smaller values of obtained for gels may suggest a slight decrease in local viscosity in this medium compared to undiluted methanol resulting from the condensation of positively charged species (Li$^+$ and product of the electrode process) on the ionized carboxylic groups of acrylic acid incorporated in the polymeric chains, even if the environment is not very ionic [50].

Aerogels

Aerogels are extremely porous materials that have been produced via sol-gel processing and supercritical drying [74,75]. They are characterized by a low density, very high surface area, translucency or transparency to visible light, low thermal conductivity, low sound velocity and complex microstructure [76-79]. Aerogels are being studied for a variety of applications mostly as novel insulators but also as

Cherenkov detectors, catalysts and catalyst supports, filters, membranes and acoustic delay lines. Most of the work in this area has been done on SiO_2 aerogels. Aerogels of Al_2O_3, TiO_2, ZrO_2, MgO and mixed oxides [80] have been prepared. Because of their distinct electrochemical applications, we will focus here on two aerogels: TiO_2 and carbon.

TiO_2

The morphology of the TiO_2 aerogels has been characterized in terms of two length scales. Typical morphology constitutes of 5 nm diameter, rough, crystalline nanoparticles of anatase closely packed into mesoaggregates near 50 nm in size. The mesoaggregates are, in turn, packed to a loosely linked structure with an overall porosity of 80%. The total surface area of these aerogels is attributed to the sum of the surfaces of the nanoparticles [61-87]. Schematic representation of this structure is given in Figure 8 [87]. This morphology was determined by using a variety of techniques that include Small Angle Neutron Scattering (SANS), Nitrogen Adsorption Isotherm (NAI) which measures the pore distribution, Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller isotherm (BET), and X-ray Diffraction (XRD). Two major applications of interest to electrochemists that use nanocrystalline TiO_2, either in the form of an aerogel or xerogels which have similar microstructure but are synthesized without the use of supercritical drying, involve photocatalytic applications targeted at solar-energy utilization, either in the form of photovoltaic devices or photocatalytic decomposition of pollutants. Below we discuss with some detail the photovoltaic application in the context of present attempts to understand the charge transport mechanisms in these systems.
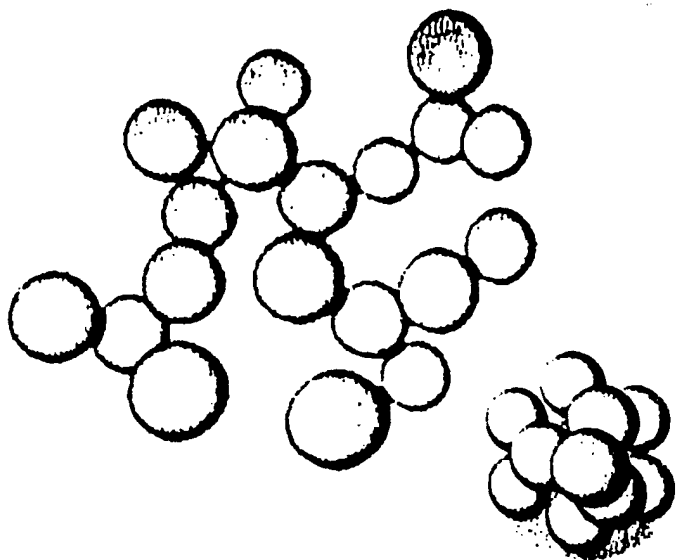
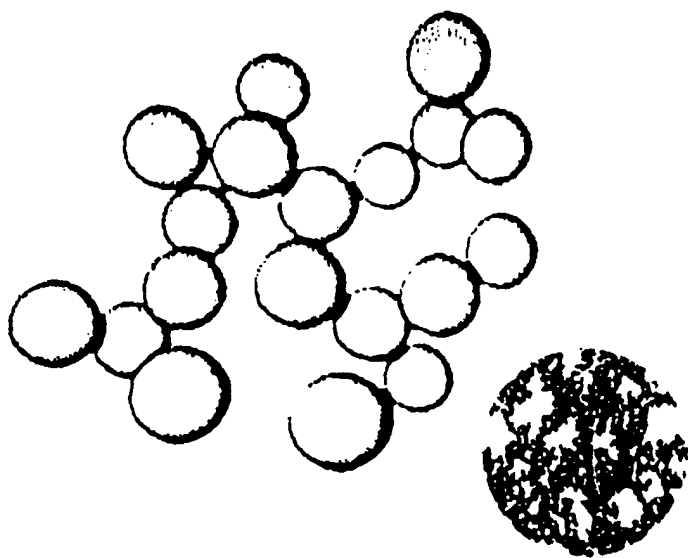**Figure 8.** Schematic representation of the structure of TiO_2 aerogel.

Figure 9. Schematic representation of the structure of carbon aerogel.

Carbon

Carbon aerogels were synthesized by critical point drying of organic gels followed by controlled pyrolysis [88]. The general morphological features of carbon aerogels is shown in Figure 9 [89-91]. The grains consist of a network of carbon filaments, depicted in the

Figure as a percolation cluster. For low catalyst ratio, the grains are distinct with an approximate surface area of 550 m^2/g. For high catalyst ratio, the cross section between the grains is of the order of the grain diameter, and the grains form a more filamentous structure with a higher surface area that can reach 800 m^2/g. It has been suggested [89] that the primary electronic conduction mechanism is associated with the grain interconnectivity rather than with the disorder internal to the grains. It was shown [90] that the predominant low temperature electronic conduction mechanism is Coulomb Gap Variable Range Hopping. This was determined through fit of the low temperature conductivity to eq. 21 and was collaborated by low temperature magnetoresistance measurements.

Applications

We will conclude by describing some important applications in which transport properties of gels and aerogels play a significant role.

Liquid-Junction Photovoltaic Solar Cells with Nanocrystalline Semiconductors

One of the most interesting applications in the context of the systems that we are discussing here are solar cells with the photoactive electrode made of TiO_2 xerogels sensitized by an organic dye, in contact with a gel electrolyte [91]. The work by O'Regan and Grätzel [92] has demonstrated that high power conversion efficiency and stability can be attained by dye-sensitized photoelectrochemical photovoltaic cells that are based on nanocrystalline porous TiO_2 sensitized by Ru-containing metal-organic dye complexes. Since this announcement, considerable work was conducted throughout the world - first to confirm the results [93], and then to improve and understand the physics and chemistry that takes place in these systems [94-95]. Schematic representation of such a cell is shown in Figure 10. Light is absorbed by the dye separating electron-hole pairs. Time resolved measurements clearly demonstrate that electron transfer takes place from the photoexcited dye to the TiO_2 nanoparticle [97-99]. The time scale for this transfer is reported to be faster than 50 fs [97]. This negatively charged "hole" slows down considerably the back reaction to produce high quantum efficiency charge separation. The

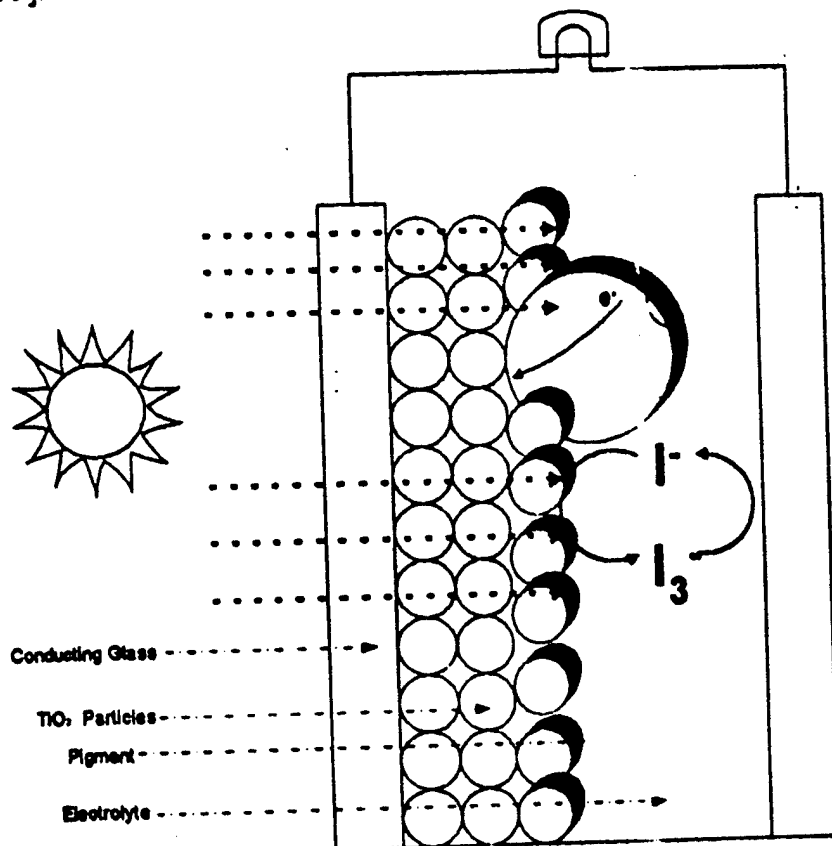recombination rates are reported to be in the μsec range [98,99].

Figure 10. Schematic representation of a dye-sensitized photoelectrochemical photovoltaic cell.

The mechanism of the electron transport in this system and in particular the particle-particle transport is less clear. Intensity modulated photocurrent spectroscopy (IMPS) and time-resolved photocurrent measurements [100-104] indicate that the interparticle electron transport is rate limiting. The reported diffusion coefficient is around 10^{-6} cm^2/sec [101,102] and changes with light intensity. This is in contrast to the diffusion coefficient of electrons in rutile estimated at 10^{-2} cm^2/sec [101]. The most common approach to account for these observations is that the conduction is dominated by thermally assisted hopping through trap states. Nelson [105] developed a continuous-time random-walk model to account for these observations. The model assumes a given energetic trap distribution, and that the electrolyte screens out Coulombic forces. It allows the electrons to move within the semiconductor in a Brownian diffusion. It assumes

that the traps are localized at the surface with a concentration of $10^{14}/cm^2$.

Electrochemical Capacitors

Electrochemical capacitors have been commercially available for several years. They are characterized by a relatively very large density of stored charge and relatively large effective series resistance, esr. A comprehensive review of electrochemical capacitors can be found in reference [106]. In the simplest form of electrochemical capacitors we rely on the chemically inert double layer capacity which for most conductive solids in contact with aqueous electrolytes is around $10 - 20 \mu F/cm^2$, yet the concept was extended to surface redox processes with interfacial capacitance of $200 \mu F/cm^2$ and more. It has been demonstrated that carbon aerogels can serve as efficient supercapacitors [107].

Polymeric Gels as Electrolytes for Lithium-ion Batteries

Two major strategies have been employed in the development of solid polymer electrolytes for lithium batteries in recent years. One is the construction of solid polymer electrolytes with supramolecular architectures, which intrinsically enhance mechanical strength. These materials usually exhibit relatively low to medium conductivity levels, typical for polymeric electrolytes, but may be applied as very thin films. The other direction is to develop highly conductive materials via the cross-linking of mobile chains to form networks, which are then swollen by lithium salt solutions and form gel electrolytes. Thus, the matrix in which the ion transport occurs is liquid-like [108].

Since the segmental motion of the polymer host matrix has been identified as the main parameter controlling conductivity [109], "plasticizers" – organic solvents with dissolved lithium salt are used to swell the polymeric network, and they improve the conductivity of the system. To be effective, relatively large weight fractions of solvents like propylene carbonate (PC), or ethylene carbonate (EC), are required. Solid polymer electrolytes, SPE, networks with a moderate cross-link density can be swollen with those organic solvents (excellent solvents of Li salts) to a large extent. These gel polymer electrolytes combine

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the mechanical properties of a swollen polymer network with the high ion conductivity of liquid electrolytes. For example, the comparison of conductivity of a "dry" network of the phosphazene-based SPE (6 wt.% $LiClO_4$, Li/O = 0.028) with the same polymeric network swollen with propylene carbonate (11 wt.% $LiClO_4$, 60 wt.% PC, Li/O = 0.043) shows that at room temperature conductivity of the gel electrolyte is more than two orders of magnitude higher than that of the "dry" electrolyte [110].

Acknowledgment

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